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Day-of-Week Patterns of Particulate Matter and Its Chemical Components at Selected Sites in California

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ABSTRACT

This paper analyzes day-of-week variations in concentrations of particulate matter (PM) in California. Because volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) are not only precursors of ozone (O_3) but also of secondary PM, it is useful to know whether the variations by day of week in these precursors are also evident in PM data. Concentrations of PM $\leq$10 μm (PM_{10}) and $\leq$2.5 μm in aerodynamic diameter ($PM_{2.5}$) were analyzed. PM concentrations exhibit a general weekly pattern, with the maximum occurring late in the workweek and the minimum occurring on weekends (especially Sunday); however, this pattern does not prevail at all sites and areas. PM nitrate (NO_3^-) data from Size Selective Inlet (SSI) samplers in the South Coast Air Basin (SoCAB) tend to be somewhat lower on weekends compared with weekdays. During 1988–1991, the weekend average was lower than the weekday average at 8 of 13 locations, with an average decrease of 1%. During 1997–2000, the weekend average was lower than the weekday average at 10 of 13 locations, with an average decrease of 6%. The weekend averages are generally lower than weekday averages for sulfates, organic carbon, and elemental carbon. Because heavy-duty trucks typically represent a major source of elemental carbon, the weekend decrease in heavy-duty truck traffic may also result in a decrease in ambient elemental carbon concentrations.

IMPLICATIONS

Some researchers have postulated that the higher O_3 observed on weekends in several California cities is caused by lower weekend NO_x emissions, primarily from reduced trucking activity. While a cause-and-effect relationship is being fully investigated with data analysis, emission inventory, and O_3 modeling studies, it is useful to consider the control implications of day-of-week patterns in PM and its components. This investigation concludes that particle mass, elemental carbon, and nitrates are lower on weekends, consistent with reduced diesel PM and NO_x emissions. While it was not possible to demonstrate a cause-and-effect relationship, it is important to consider all pollutants when formulating control strategies.

INTRODUCTION

Airborne particulate matter (PM) is not a single pollutant but rather a mixture of primary and secondary aerosols containing many subclasses of pollutants, with each subclass potentially containing many different chemical species.[1] In California, the proximity of a location to a variety of sources, in addition to the diurnal and seasonal variations in meteorological conditions, causes the size, composition, and concentration of PM to vary in space and time.[2] Although PM pollution still remains the most serious and complex air pollution problem facing both scientific communities and regulatory agencies,[3] exceedances of PM standards have become less frequent in California (Table 1). Over the 10-yr period from 1990 to 2000, despite large increases in population (12%) and the number of vehicle miles traveled (15%), California has been able to achieve both significantly cleaner air and major economic growth (28% increase in gross state product).[4]

Particles less than 2.5 μm in aerodynamic diameter ($PM_{2.5}$) are generally referred to as "fine" and those from 2.5 to 10 μm diameter (PM_{10}) as "coarse." The selection of PM_{10} as an indicator was based on health considerations and was intended to focus regulatory concern on those particles sufficiently small to enter the thoracic region of the lungs. California's recent scientific review of the health effects literature resulted in a lowering of the existing PM_{10} annual-average standard from 30 to 20 $\mu g/m^3$ and the establishment of a $PM_{2.5}$ annual-average standard of 12 $\mu g/m^3$.[5] The standards are based on epidemiologic studies showing associations between ambient PM_{10} and $PM_{2.5}$ levels and increased mortality and morbidity. They complement the existing 24-hr PM_{10} standard of 50 $\mu g/m^3$, and all standards are never to be exceeded.

In addition to falling into different size ranges, fine and coarse particles differ in formation mechanisms, chemical composition, sources, and exposure relationships.[1] Fine PM is derived from combustion material that has volatilized and then condensed to form primary PM, and from precursor gases (e.g., sulfur dioxide [SO_2], nitrogen oxides [NO_x], and certain organic compounds) reacting in the atmosphere to form secondary PM. Coarse PM,

Table 1. Calculated exceedances of ambient standards for PM_{10} in selected air basins during two periods in California.

Region	California 24-hr PM_{10} Standard Average Exceedances		National 24-hr PM_{10} Standard Average Exceedances	
	1988–1990	1998–2000	1988–1990	1998–2000
Sacramento Valley Air Basin	99	57	0	2
San Francisco Bay Area Air Basin	78	32	2	0
San Joaquin Valley Air Basin	249	156	31	5
South Coast Air Basin	294	230	27	2

Note: The number of exceedances is "calculated" as if sampling was done daily.

in contrast, is formed by crushing, grinding, and abrasion of surfaces, which forms particles that are then suspended by wind or by anthropogenic activities such as construction, mining, and agriculture. As the particles respond to variations in their atmospheric environment, their chemical and physical properties can change by accumulation of atmospheric gas-phase chemical reaction products or through heterogeneous reactions with gas-phase species.

Gaseous SO_2 emitted from fossil fuel combustion, as well as organic species emitted from both anthropogenic and biogenic sources, can react in the atmosphere to form particulate sulfates or secondary organic aerosols, respectively. In fresh NO_x emissions, which primarily consist of nitric oxide (NO) and smaller amounts of nitrogen dioxide (NO_2), the NO undergoes reactions with ozone (O_3) and peroxy radicals to form additional NO_2. The NO_2 can be directly converted to nitric acid (HNO_3) via a homogenous gas-phase reaction with the hydroxyl radical. This is the principal formation mechanism for HNO_3 in the daytime.[1] The major chemical loss process for gas-phase HNO_3 is its reaction with gaseous ammonia (NH_3) to form ammonium nitrate (NH_4NO_3). This reaction, which is reversible, is believed to be the major source of $PM_{2.5}$ nitrate (NO_3^-) aerosol in California's urban air.[2]

The atmospheric chemistry leading to formation of particulate NO_3^- is quite complex, because it depends on the concentrations of many intermediate species (including NH_3 and free radicals). Ambient concentrations of secondary particles are not necessarily proportional to the concentrations of the precursor emissions because the rates at which they form and their gas/particle equilibria may be controlled by factors other than the concentration of the precursor gas. The rate of NO_x oxidation and the branching ratio between inorganic and organic nitrates depend on the specific environmental conditions in addition to reactant concentrations.[6]

Until recently, it was assumed that the end product of the tropospheric NO_x was HNO_3. However, recent research[7] has shown that HNO_3 on a surface can react with NO to regenerate NO_2, which can then form particulate NO_3^-. Preliminary modeling studies[7] suggest that this reaction may increase the formation of particulate NO_3^- and that existing models underestimate the benefit of NO_x controls for reducing PM and O_3. Ongoing research by the same group will focus on providing a more complete understanding of the effect of heterogeneous nitrogen chemistry on O_3 and particle formation. The information gained in this research may have very serious implications as to the effectiveness of control strategies for both O_3 and PM.

Fine particles typically are comprised of sulfate (SO_4^{2-}), NO_3^-, ammonium (NH_4^+), elemental carbon, organic compounds, and a variety of other compounds. Elemental carbon has a chemical structure similar to impure graphite and is emitted directly by sources. Organic carbon either can be emitted directly by sources (motor vehicles, wood smoke, and food cooking operations) or can be the result of the condensation of low-vapor-pressure products of the gas-phase reactions of hydrocarbons onto the existing aerosol (secondary organic carbon). Although the mechanisms and pathways for forming inorganic secondary PM are fairly well known, those for forming secondary organic PM are not as well understood. Ozone and the hydroxyl radical are thought to be the major initiating reactants.

Temperature is a factor in the chemistry that produces secondary PM. Urban heat islands are among the most robust and well-documented of anthropogenic meteorological effects, and it seems physically plausible that in a massively urbanized area such as the South Coast Air Basin (SoCAB), there could be many human influences that could potentially influence the surface temperature. To investigate possible day-of-week variations in temperature, Blier et al.[8] conducted a study to investigate anthropogenic influences on day-of-week variation in SoCAB meteorological conditions. Mean hourly temperature data from 11 sites, well distributed through the region of the SoCAB, were analyzed.

The results indicate a gradual increase in the mean smog season daily-maximum temperature during the 1949–1994 period of approximately 2 °F can be observed for both weekdays and weekends. This suggests that the urban heat island effect intensified during the 11-yr period of investigation; however, there did not appear to exist a clear day-of-week temperature effect. It was concluded that if a day-of-week temperature effect does exist in the SoCAB, it is quite weak and therefore not likely to be of particular importance to air quality management efforts.

Blier et al.[8] also examined relative humidity (RH) data for an anthropogenic weekday/weekend effect. Although their results indicated a slight average increase in RH on weekends (0.4%), unlike the temperature analysis, there was no consistency in sign between either the various stations or the different times of day. In addition, the standard deviations were much larger than the weekday/weekend RH differences. Thus, no day-of-week signal was evident for RH.

Limited studies[9] indicate that there may be changes in the secondary components because of increased oxidants during weekends. Thus, given the contribution of NO_x and volatile organic compounds (VOCs) to secondary PM formation, it would be useful to know whether the variations by day of week in these precursors are evident in PM data.

PM-RELATED DATA RESOURCES

California's PM_{10} monitoring program began in 1984, and the network currently has more than 150 sites. To assess the nature and extent of the $PM_{2.5}$ problem in California, a network of 82 Federal Reference Method (FRM) samplers was deployed in 1998–1999. The routine particle data used in this study were available from the U.S. Environmental Protection Agency's (EPA) Aerometric Information and Retrieval System (AIRS), through which data are reported from California's routine PM monitoring programs (i.e., $PM_{2.5}$-FRM, PM_{10}-SSI, Dichot, and TEOM samplers operated by the California Air Resources Board [CARB] and local air pollution control districts [Figure 1]). Table 2 lists routine monitoring PM networks in California and associated information on start and end year of operation, cut-points, flow rates, sampling frequency, species, and number of sites.

With the routine monitoring program, samples of PM_{10} are collected over a 24-hr period using a high-volume sampler equipped with an SSI (PM_{10}-SSI) or using a dichotomous (Dichot) sampler. Samples are usually collected from midnight to midnight every sixth day. Compositional analysis currently provides measurements of NO_3^-, SO_4^{2-}, NH_4^+, chloride (Cl), and potassium (K) for selected sites. The dichotomous sampler, or virtual impactor, uses a low-volume PM_{10} inlet followed by a split in the flow stream that separates particles into two separate fractions: fine particles ($PM_{2.5}$) and coarse particles (those having diameters 2.5–10 μm). The sum of the fine and

Figure 1. FRM-$PM_{2.5}$ and dichotomous sampling locations.

Table 2. California PM monitoring networks.

Sampler	Cut-Points (μm)	Flow Rates (L/min)	Time Avg.	Species	No. of Sites
FRM (1999–present)	2.5	16.7	24-hr	—	82
SSI (1984–2000)	10	~1000	24-hr	Ions	~150
TEOM (1994–2000)	10	16.7 → 3	1-hr	—	35
Dichot (1988–2000)	2.5, 10–2.5	15, 1.7	24-hr	Elements	20
CADMP (1988–1998)	2.5, 10	20	12 → 4-hr	Ions, acids	10 → 5

coarse fractions provides a measure of total PM_{10} from the Dichot sampler.

Data from the California Acid Deposition Monitoring Program (CADMP) and the PM Technical Enhancement Program (TEP2000) were also used. The CADMP sampler[10] was designed for collection of particulate species in two size fractions ($PM_{2.5}$ and PM_{10}) and acidic gases. The CADMP network was established in early 1988 to determine the spatial and temporal patterns of acidic pollutant concentrations in California. In September 1995, the CADMP network was reduced to five monitoring sites located primarily in urban areas (i.e., Azusa, Bakersfield, Long Beach, Los Angeles, and Sacramento), and the sampling was reduced to $PM_{2.5}$ only in once every sixth day. The CADMP monitoring was terminated in May 2000.

In 1995, a 1-yr PM_{10} Technical Enhancement Program (PTEP) monitoring[11,12] was conducted at six sites: downtown Los Angeles, Anaheim, Diamond Bar, Rubidoux, Fontana, and San Nicolas Island. At each location, the sampling equipment was deployed to collect fine and coarse particulate fractions for speciation as well as gas-phase HNO_3, elemental carbon, NH_4^+, and metals. To better characterize the emissions, formation, and transport of fine PM across the SoCAB, the South Coast Air Quality Management District conducted an additional comprehensive Technical Enhancement Program (TEP2000).

TEP2000 sampling was performed both upwind and downwind of significant NH_3 sources in the SoCAB. Diamond Bar is a representative area at the urban fringe and is upwind of NH_3 sources (dairy farms). Fontana and Rubidoux represent downwind receptor areas and are also downwind of NH_3 sources. The Los Angeles and Anaheim sites are representative of primary vehicle and stationary source emissions areas. The monitoring program included 24-hr sampling on a one-in-three-day sampling schedule from August 1998 through July 1999. Every-day sampling at three of the sites (Los Angeles, Anaheim, and Rubidoux) during the peak October–November period was also conducted.

The CARB and local air pollution control districts have collected fine PM data in California since 1989. A recent review of these data[13] indicated that the $PM_{2.5}$ database that has resulted from several long-term monitoring programs is in agreement with FRM samplers. These alternate data sources are a valuable resource for assessing the nature of the fine particulate problem in California and will be useful in the development of plans to attain the new national $PM_{2.5}$ ambient air quality standards.

METHODOLOGY

The basic approach was to analyze ambient PM_{10} and $PM_{2.5}$ concentrations for day-of-week patterns. Statistical tests were performed to provide an indication of the magnitude of the systematic differences in particle mass between days of the week relative to random day-to-day variation. Where significant differences exist, additional analyses were undertaken to determine which particle species contribute to the differences. In general, long-term data records increased the statistical confidence associated with the observed differences in the mean values, because the standard errors associated with the mean values scale at $n^{-1/2}$, where n is the number of observations used to calculate the mean. The model used to determine the standard errors accounted for variability by year and by day of week, so these were not included in the error term.

Day-of-week PM data were compared for different days of the week by examining confidence intervals around the day-of-week means. Because of limited space, the results of all the intervals for all sites are not included in this paper. Figures 2-6 provide results for pairwise comparisons between days of the week for some sites at approximate 90–95% confidence levels. To confirm the statistical results, the SAS general linear model (GLM) procedure was used to perform analysis of variance on day-of-week means, including fixed effects for month crossed with year. To stabilize the error variance and reduce the effect of extreme observations, the data were transformed according to the relationship $y = \log(x)$, rendering the transformed data as normally distributed because the original data are log-normally distributed. The results are similar to those performed by comparing confidence intervals.

DISCUSSION OF RESULTS

Day-of-Week Analysis of PM Mass

Because clean air typically flows inland from the Pacific Ocean, the percent of days exceeding the California 24-hr standard is generally lower along the coast than in inland areas. In areas of extensive anthropogenic influence, PM

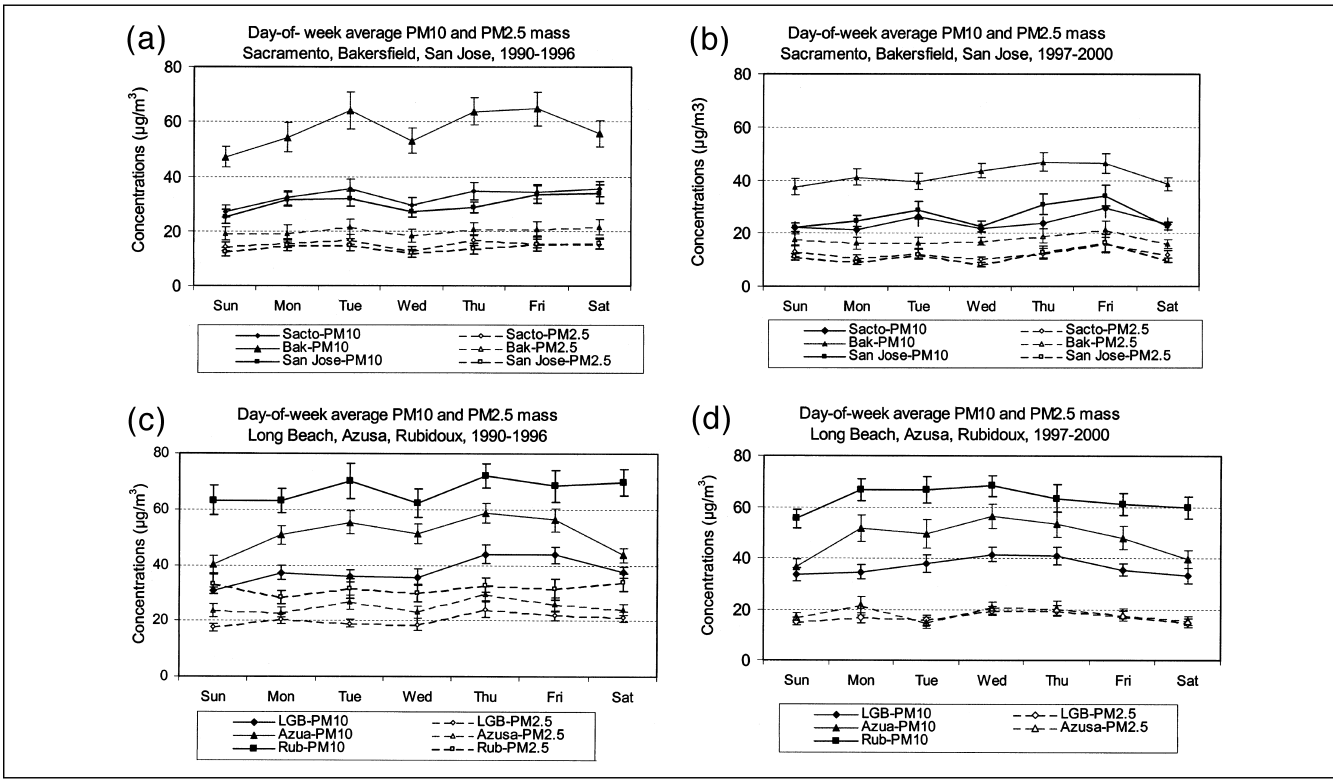

Figure 2. (a) Day-of-week average SSI-PM_{10} and Dichot $PM_{2.5}$ at Sacramento, Bakersfield, and San Jose, 1990–1996. (b) Day-of-week average SSI-PM_{10} and Dichot $PM_{2.5}$ at Sacramento, Bakersfield, and San Jose, 1997–2000. (c) Day-of-week average SSI-PM_{10} and Dichot $PM_{2.5}$ at Long Beach, Azusa, and Riverside-Rubidoux, 1990–1996. (d) Day-of-week average SSI-PM_{10} and Dichot $PM_{2.5}$ at Long Beach, Azusa, and Riverside-Rubidoux, 1997–2000.

concentrations tend to increase with distance downwind because of fresh emissions and gas-to-particle conversion.[14] Table 3 displays the average PM_{10} concentrations by day of the week for 20 sites in the SoCAB from 1998 to 2000. Analyses of PM_{10} mass from the SSI samplers show that Sundays are the lowest PM_{10} days of the week at 12 of 20 locations, often significantly different from midweek; however, the pattern is not statistically significant at all sites. The PM_{10} Sunday minimum might be caused by the lower car and truck traffic on Sundays compared with midweek and the associated decrease in road dust and emissions of PM and PM precursors. The Saturday mean

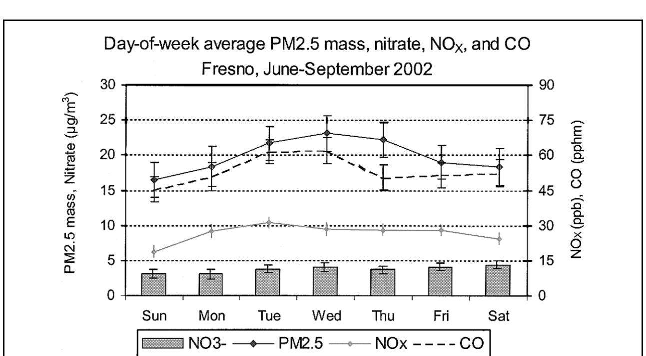

Figure 3. Day-of-week average continuous $PM_{2.5}$ mass, NO_3^-, NO_x, and CO at Fresno, June–September 2002.

concentration is generally comparable to weekday concentrations. A majority (15 of 20) of sites show Wednesday as having the highest PM_{10} during the week in 1998–2000. At 14 of 20 sites, the difference from Sunday to Wednesday was significant with approximately 95% confidence.

The history and spatial distribution of day-of-week differences in ambient $PM_{2.5}$ and PM_{10} concentrations were described through the analysis of a decade of measurements from selected urban sites. Figures 2a and 2b show day-of-week average SSI-PM_{10} and Dichot $PM_{2.5}$ at the Sacramento, Bakersfield, and San Jose sites in the 1990–1996 and 1997–2000 periods. The two periods were selected to separate the changes associated with the implementation of reformulated gasoline regulations in 1995. Federal reformulated gasoline was introduced in Los Angeles beginning in the spring of 1995, and California cleaner-burning gasoline was introduced statewide in the spring of 1996.[15]

Day-of-week PM_{10} mass generally follows the same pattern as $PM_{2.5}$ mass, with Sunday showing the lowest PM concentrations, followed by Wednesday, and then Saturday. Analyses of PM_{10} and $PM_{2.5}$ data from the SSI and Dichot samplers at Long Beach, Azusa, and Riverside-Rubidoux show the same pattern in the 1990–1996 period

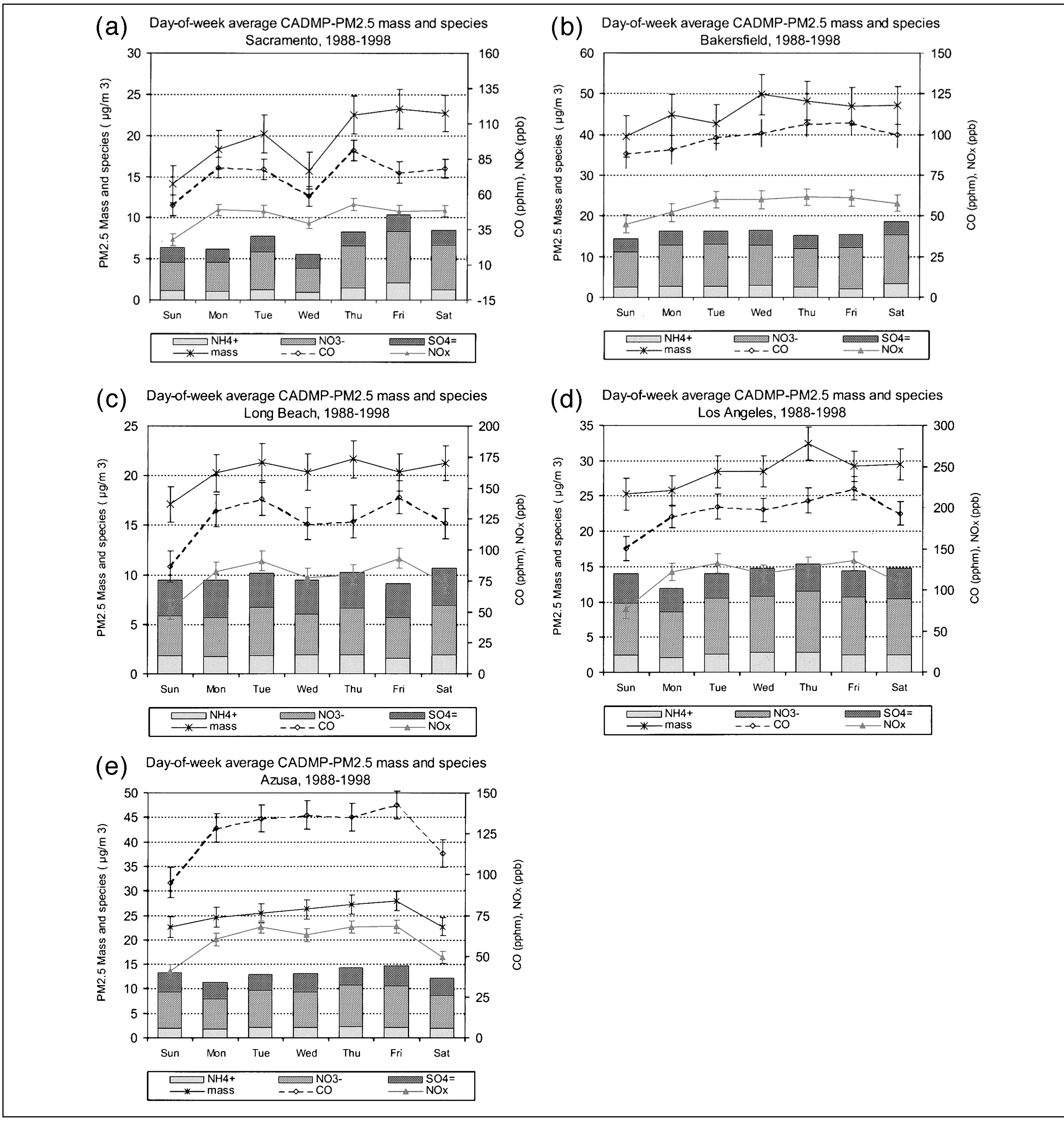

Figure 4. (a) Day-of-week average CADMP-$PM_{2.5}$ mass and species at Sacramento, 1988–1998. (b) Day-of-week average CADMP-$PM_{2.5}$ mass and species at Bakersfield, 1988–1998. Unexplained portion of the measured PM mass is organic compounds, water, and trace metals. (c) Day-of-week average CADMP-$PM_{2.5}$ mass and species at Long Beach, 1988–1998. (d) Day-of-week average CADMP-$PM_{2.5}$ mass and species at Los Angeles, 1988–1998. (e) Day-of-week average CADMP-$PM_{2.5}$ mass and species at Azusa, 1988–1998.

(Figure 2c); however, the Wednesday dip disappears in the 1997–2000 period (Figure 2d). During 1997–2000, after the introduction of reformulated gasoline regulations, mean fine PM concentrations decreased on all days, regardless of the day of the week, at virtually all sites. This decrease is expected because these regulations were aimed to reduce smog-forming pollutants such as NO_x and VOCs.

Day-of-Week Analysis of PM Species

Compared with the rest of the nation, nitrates in California represent a larger fraction of PM mass, more than one-fourth the average annual fine mass.[14] Secondary pollutant formation is influenced by a combination of precursor pollutant concentrations and weather conditions. NO_x conversion to NO_3^- is very sensitive to meteorological conditions, because formation rates must

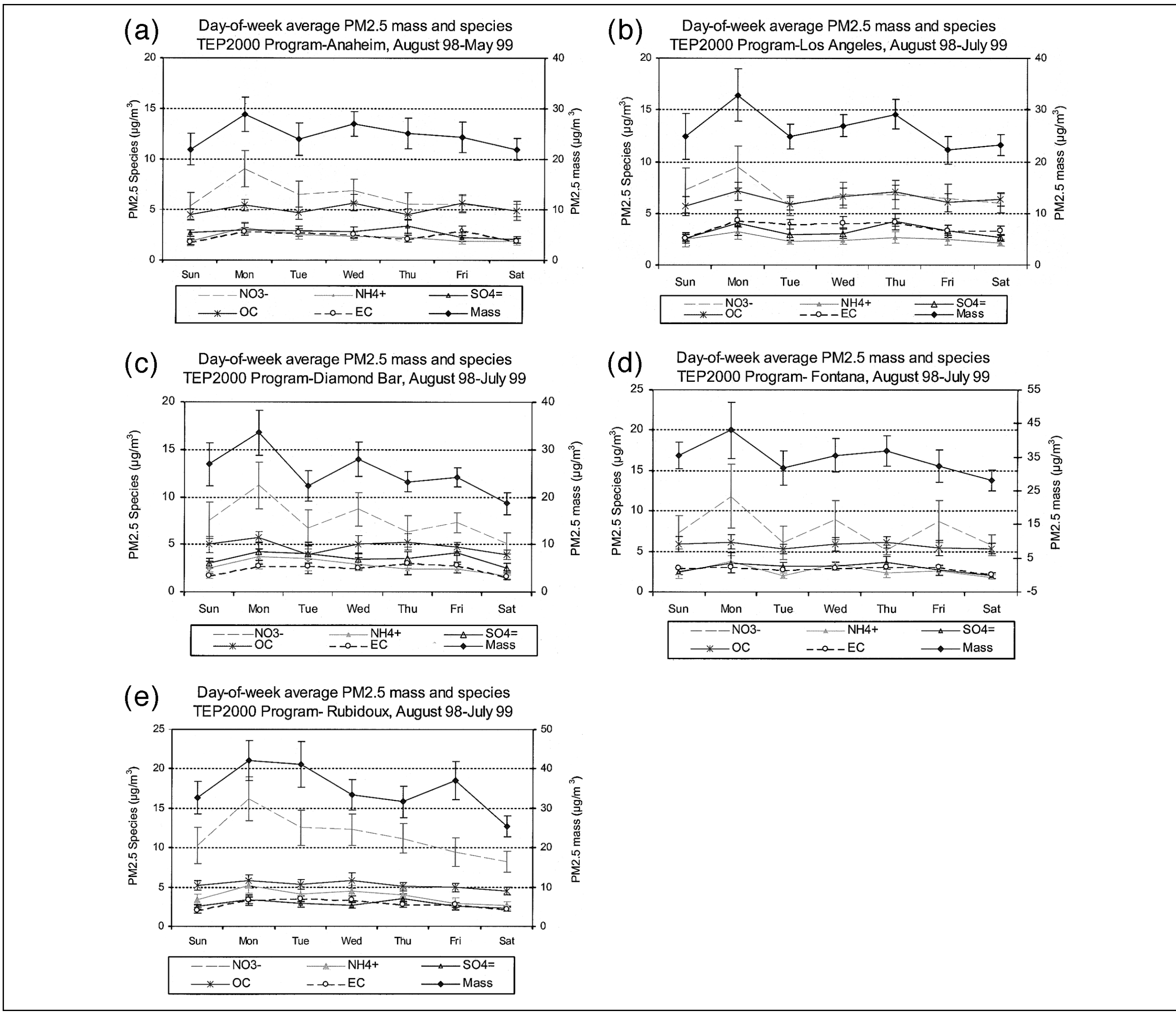

Figure 5. (a) Day-of-week average TEP2000-$PM_{2.5}$ mass and species at Anaheim, August 1998–May 1999. (b) Day-of-week average TEP2000-$PM_{2.5}$ mass and species at downtown Los Angeles, August 1998–July 1999. (c) Day-of-week average TEP2000-$PM_{2.5}$ mass and species at Diamond Bar, August 1998–July 1999. (d) Day-of-week average TEP2000-$PM_{2.5}$ mass and species at Fontana, August 1998–July 1999. (e) Day-of-week average TEP2000-$PM_{2.5}$ mass and species at Riverside-Rubidoux, August 1998–July 1999.

compete with dissociation back to gases, so that NO_3^- is generally a cool-wet (e.g., winter) phenomenon in California.

A continuous PM monitoring method such as a beta attenuation monitor (BAM) and continuous PM-NO_3^- analyzer provide additional insight into the nature of the particulate problem and reduce the uncertainties associated with less than daily sampling frequencies.[16] As part of the exposure component of the Fresno Asthmatic Children's Environment Study, hourly average CO, NO_x, NO_3^-, and $PM_{2.5}$ mass are available at a site in Fresno from June through September 2002 (Figure 3). Day-of-week BAM-$PM_{2.5}$ mass generally follows the same pattern as CO and NO_x, with Sunday showing the lowest concentrations.

Table 4 displays the annual-average SSI PM_{10} NO_3^- concentrations at 13 sites in the SoCAB. The highest annual average particulate NO_3^- concentrations are usually observed at Rubidoux-Riverside and Fontana. Examination of the 1997–2000 results indicates a weekly pattern with the maximum particulate NO_3^- concentrations generally occurring on a weekday. At 10 of the 13 locations, the weekend average was lower than the weekday average for PM-NO_3^-. Across all 13 sites, weekend PM-NO_3^- concentrations averaged 6% lower compared with the weekday average.

Table 4 shows two additional patterns. First, average PM-NO_3^- concentrations in 1997–2000 were lower on Sunday, Tuesday, and Saturday for almost all sites

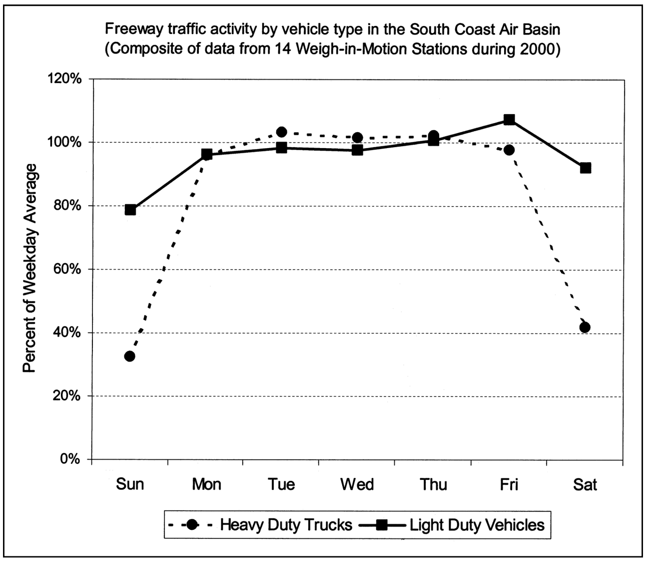

Figure 6. Freeway traffic activity by vehicle type in the SoCAB.

compared with 1988–1991. These decreases in PM-NO_3^- coincide with decreases in ambient NO_x concentrations. Second, the PM-NO_3^- data show changes by day-of-week that are highly variable. For example, at Los Angeles-North Main, Tuesday showed a strong decrease from 1988–1991 to 1997–2000, while Wednesday showed a strong increase followed by a decrease on Thursday. These day-of-week differences in trend have no obvious explanation and raise questions about the adequacy of the available data. Nitrate particle losses in current sampling methods are very high because of volatilization of NH_4NO_3 under changing conditions of temperature and RH during sampling and transport of the filter samples. These losses can be as large as 50%, resulting in an underestimation of ambient NH_4NO_3 particles.[17] Results of a study indicate that annual average NO_3^- losses in the SoCAB do not show significant spatial variation.[18] In general, NO_3^- losses were high in summer and low in winter. Thus, this bias should result in systematic measurement error for all days, hence not affecting day-of-week patterns.

Examination of $PM_{2.5}$ mass and species at CADMP sites show that Sunday is the lowest day of the week at four of the CADMP sites, and generally the day-of-week pattern of the NO_3^- and NH_4^+ data is associated closely with the $PM_{2.5}$ mass data (Figures 4a–e). These data indicate the importance of particulate NO_3^- as a component of fine particulate concentrations, accounting for ~30–40% of the annual-average fine particle mass. Particulate SO_4^{2-} concentrations are typically lower than in many other parts of the country and sufficient NH_3 is available at most times and locations to allow the formation of particulate NH_4NO_3. It should be noted that the unexplained portion of the measured PM mass in the CADMP database is elemental and organic carbon compounds, water, and trace metals.

Day-of-week patterns of the CADMP-$PM_{2.5}$ data follow relatively the same pattern as NO_x and CO data. This similarity, combined with the facts that the vast majority of CO emissions and much of the NO_x emissions come from light-duty vehicles, indicates that motor vehicles, whether by direct emissions, re-entrainment processes, or secondary formation from gaseous emissions, contribute appreciably to ambient PM concentrations in California.

Fisher's least significant difference method[19,20] is used to analyze for a significant day-of-week effect on $PM_{2.5}$ mass and species at the TEP2000 sites. This procedure is a simple *t* test. In this case, the Fisher method produces intervals that contain the true difference between each pair of means with a probability of 95%. A $PM_{2.5}$ maximum occurs on Monday at many sites (Figures 5a–e). This "Monday effect" is also evident at several sites for NO_3^- and NH_4^+. The weekend averages are generally lower than weekday averages for nitrates, sulfates, organic carbon, and elemental carbon. Because heavy-duty trucks typically represent a major source of elemental carbon, the Sunday decrease in heavy-duty truck travel may also result in a decrease in ambient elemental carbon concentrations.

Analysis of the PM species indicates that NH_4^+ and NO_3^- show a strong spatial variation with low concentrations at coastal locations and high concentrations at inland locations. This is partly because of transported precursor emissions of NO_x having more time to convert to HNO_3. Excess NH_3 is present at most times (high NH_3 emissions in the air basin originate near Chino from agricultural and livestock operations); thus, any gas-phase HNO_3 formed usually will be driven quickly into the aerosol phase. Sulfate concentrations do not show strong spatial variations. Although elemental and organic carbon concentrations do not show a strong spatial variation, the Los Angeles-North Main site has the highest elemental and organic carbon concentration because it is the site with highest traffic in SoCAB.

Emissions and Relationships to Weekend and Weekday Concentrations

The results of emission estimates, using EMFAC2000 version 2.02, indicate that on-road mobile sources are the single largest source category of reactive organic gas, NO_x, and CO, accounting for approximately 50, 60, and 80% of average daily emissions, respectively, in the SoCAB. As part of a larger investigation of the PM weekend effect, patterns in traffic data were analyzed and compared with patterns in air quality data. These analyses were limited to the SoCAB, but they yielded significant results that may

Table 3. Average annual PM_{10} concentrations at locations in the SoCAB based on measured data from SSI samplers, 1998–2000.

			Summary Statistics for PM_{10} Mass: 1998–2000 in the SoCAB						
Site	**County**		**Sunday**	**Monday**	**Tuesday**	**Wednesday**	**Thursday**	**Friday**	**Saturday**
Azusa	Los Angeles	Mean	35.6	51	49	**58.3**	53.4	42.7	45
		Standard error	2.69	4.74	4.65	4.52	3.78	3.94	3.64
Burbank–West Palm Avenue	Los Angeles	Mean	34.6	40.7	40.1	**46.4**	40.5	39	35.9
		Standard error	2.63	3.09	3.33	3.19	2.37	3.24	2.7
Hawthorne	Los Angeles	Mean	32.4	31.8	35.2	39.3	**40.3**	31.3	32.2
		Standard error	1.97	2.18	3.48	2.72	2.44	2.58	2.6
Los Angeles–North Main Street	Los Angeles	Mean	35	41.8	40.1	**50.3**	43.7	36.9	37.3
		Standard error	2.62	3.55	3.48	3.49	2.71	2.2	2.76
North Long Beach	Los Angeles	Mean	32.5	38.9	37	**41.6**	39.6	30.4	35
		Standard error	2.3	3.88	3.89	3.02	3.05	2.02	3.71
Santa Clarita–County Fire Station	Los Angeles	Mean	29.1	31.1	35.1	**38.5**	36.7	34.5	29.7
		Standard error	1.98	2.92	4	2.95	2.62	2.97	2
Anaheim–Harbor Boulevard	Orange	Mean	34.4	41.4	39.1	**46.5**	44	42.9	36.3
		Standard error	2.49	4.56	4.16	3.56	4.42	6.51	4.8
El Toro	Orange	Mean	28.7	33.7	30.5	34.9	**38.9**	32.8	29.2
		Standard error	2.24	2.57	3.15	2.82	4.3	2.72	1.87
Mission Viejo–26081 Via Pera	Orange	Mean	28.1	27.4	26.2	29.1	**30.3**	26.1	29.2
		Standard error	3.11	1.69	2.7	2.82	1.97	3.37	4.67
Banning Airport	Riverside	Mean	24.4	28.5	30.3	**38.8**	31.5	23.5	28.7
		Standard error	2.48	3.54	3.39	3.31	2.3	2.95	4.02
Banning–Allesandro	Riverside	Mean	20.9	26.6	29.2	**34.7**	34	26.9	24.6
		Standard error	4.13	5.05	4.17	5.39	2.72	6.61	5.41
Norco–Norconian	Riverside	Mean	48.6	51.9	48.6	**56.3**	56	46.2	45.3
		Standard error	3.56	5.41	6.09	5.12	5.04	3.97	4.83
Perris	Riverside	Mean	37.7	43.7	45	**53.4**	46.5	41.3	36.8
		Standard error	3.45	4.72	5.21	3.97	3.79	4.12	2.84
Riverside–Rubidoux	Riverside	Mean	55	63.9	66.1	**69.1**	63.6	59.1	61
		Standard error	4.44	5.1	6.16	4.36	4.89	4.54	4.98
Crestline	San Bernardino	Mean	24.4	23.1	26.9	25.9	25.6	23.6	**27**
		Standard error	1.88	2.4	2.81	2.06	2.04	2.37	2.3
Fontana–Arrow Highway	San Bernardino	Mean	45.1	56.7	56	**65.6**	59.2	48.7	47.6
		Standard error	4.29	5.36	5.65	4.63	4.29	4.4	4.05
Ontario–1408 Francis Street	San Bernardino	Mean	50.2	**72.1**	60.4	69.6	61.9	46.6	46.8
		Standard error	5.03	8.32	7.48	7.84	5.25	5.49	4.37
Ontario–Airport	San Bernardino	Mean	40.6	50.8	55.1	**62.7**	58.2	43.9	41.2
		Standard error	4.81	5.9	7.86	5.68	6.1	4.25	3.07
Redlands–Dearborn	San Bernardino	Mean	36.4	45.3	47.2	**52.3**	47.6	38.2	41.5
		Standard error	3.83	5.32	5.52	3.62	3.78	4.3	4.16
San Bernardino–4th Street	San Bernardino	Mean	42.5	53.1	51.7	**59.6**	57	45.4	45.8
		Standard error	4.41	5.35	5.93	4.66	4.18	4.33	4.19

Note: Boldface indicates highest day-of-week concentration. The difference between two means is significant if the absolute difference is greater than the following: $t_{crit} \times \mathrm{sqrt}(SE_1^2 + SE_2^2)$, where t_{crit} is based on at least 30 degrees of freedom, and SE indicates standard error. Standard errors can be used to compare PM_{10} means within a site. Means within sites are approximately independent because of 1-in-6-day sampling schedules.

represent other urbanized areas. The fourteen Weigh-in-Motion stations that contributed to Figure 6 are spread somewhat uniformly throughout the SoCAB. The Weigh-in-Motion protocols identify 14 categories of vehicles. Categories 1–7 represent relatively light-duty vehicles that are predominantly gasoline-powered. Categories 8–14 represent relatively heavy-duty vehicles that are predominantly diesel-powered.

The daily volumes presented in this figure are affected most strongly by those stations that record the largest volumes. Therefore, the values represent a compromise between spatial weighting and weighting by traffic density from a basinwide perspective. The day-of-week patterns in Figure 6 do not show a midweek decrease in daily traffic volumes. These patterns, therefore, do not help explain the midweek decreases in PM mass, NO_x, and CO observed in the day-of-week patterns of the CADMP data and Table 4 for data between 1988 and 1991. Potential explanations may emerge from ongoing studies of off-road mobile sources and traffic patterns on surface streets.

Additional information on traffic patterns in the SoCAB comes from Fujita et al.,[21] a recently completed study of weekend and weekday microscale and regional emissions activity data. The results indicate that, in the urban areas of the SoCAB, surface street traffic volumes (which were dominated by light-duty vehicles) were reduced by approximately 15–30% on weekends and tended to peak around midday rather than during the weekday morning and afternoon rush hours. Further analyses show that distinct traffic patterns also exist between Saturday and Sunday. Freeway traffic volume information shows that truck and bus activities decreased by up to 80%. It was also concluded that heavy-duty truck traffic is the only on-road category that showed a different pattern of activity on freeways relative to surface streets. Heavy-duty traffic has a single peak in activity on freeways and a dual-mode peak in traffic activity on surface streets; for all other on-road categories, surface street activity is similar to freeway traffic. Fujita et al.[21] reported that nonmobile sources had little effect on variations in the VOC/NO_x ratios. Thus, although there are some small source categories that increase on weekends, the major reductions in motor vehicle activity result in large reduction in NO_x emissions on weekends.

For a region that includes the San Francisco Bay, San Joaquin Valley, and Sacramento County, traffic data analysis shows that traffic patterns differ greatly by vehicle class, day of week, and whether the location is urban or rural.[22] Analysis of traffic by day of week and vehicle class shows that at urban sites, light-duty vehicle traffic increases gradually from Monday through Friday and falls slightly on weekends. Although travel by all vehicle classes decreases on weekends, the decrease in heavy-duty truck traffic is much larger. The results also indicate that urban light-duty traffic is bimodal, with peaks during the morning and evening commuting hours. In contrast to the bimodal traffic pattern of light-duty vehicles on weekdays, heavy-duty vehicle traffic peaks late in the morning; heavy-duty vehicle traffic does not follow commuting hours. Weekend light-duty traffic has a single peak in the early afternoon. Early morning traffic, between 12:00 a.m. and 3:00 a.m., is highest on Saturday and Sunday. On weekends, heavy-duty traffic peaks on Saturday morning, declines until late that night and then increases throughout all of Sunday. All of these studies observed a decrease in heavy-duty traffic on weekends when compared with weekdays.

CONCLUSIONS

PM in the air is a significant health concern. Exposure to particulate pollution is linked to increased frequency and severity of asthma attacks and bronchitis[23] and even premature death in people with existing cardiac or respiratory disease.[24,25] Diesel PM is a carcinogen responsible for 70% of the known airborne cancer risk in California.[26]

The formation of secondary particles from gas-phase precursors is a complex process. Consequently, a one-to-one relationship between precursor emissions and ambient secondary PM concentrations is not necessarily expected. The rate of NO_x oxidation and the branching ratio between inorganic and organic nitrates are known to depend on the specific environmental conditions in addition to reactant concentrations. The partitioning of inorganic NO_3^- between gaseous HNO_3, NH_4NO_3, and nonvolatile NO_3^- is known to depend on a number of factors, such as RH, temperature, and NH_3, in a nonlinear manner. Understanding how particulate NH_4NO_3 is formed and how to effectively reduce it through controls on NO_x or NH_3 sources is a critical part of California's $PM_{2.5}$ program.

Analyses of day-of-week PM mass and species data showed the following:

- Based on 1998–2000 SSI data, average PM_{10} concentrations on Sunday were significantly lower compared with the concentrations on Wednesday at 14 of 20 locations.
- Day-of-week SSI-PM_{10} mass generally tracks the same pattern as Dichot-$PM_{2.5}$ mass, with Sunday showing the lowest PM concentrations, followed by Wednesday, and then Saturday. However, the Wednesday dip disappeared in 1997–2000 after the introduction of the cleaner-burning gasoline regulations.
- PM NO_3^- data from SSI samplers in the SoCAB tend to be somewhat lower on weekends compared with weekdays. During 1988–1991, the weekend average was lower than the weekday average at 8 of 13 locations, with an average decrease of 1%. During 1997–2000, the weekend average was lower than the weekday average at 10 of 13 locations, with an average decrease of 6%.
- Examination of $PM_{2.5}$ mass and species at CADMP and TEP2000 sites show that Sunday is the lowest day of the week at the majority of sites, and generally the day-of-week pattern of the NO_3^- and NH_4^+ data corresponds closely with

Table 4. Average annual PM_{10}-NO_3^- concentrations at locations in the SoCAB based on measured data from SSI samplers.

			Day-of-Week Average PM_{10}-NO_3^- Concentration ($\mu g/m^3$)						
Site	**Period**		**Sunday**	**Monday**	**Tuesday**	**Wednesday**	**Thursday**	**Friday**	**Saturday**
Hawthorne	1988–1991	Mean	3.5	4.65	4.9	4.86	**5.34**	3.35	4.94
		Standard error	1.07	1.07	1.07	1.01	1.05	1.03	1.05
	1997–2000	Mean	4.96	4.64	4.39	4.89	**5.21**	4.19	4.56
		Standard error	0.88	0.91	0.94	0.88	0.86	0.96	0.96
		% Change	+42	0	−10	+1	−2	+25	−8
San Bernardino–4th Street	1988–1991	Mean	12.45	**14.02**	10.23	10.06	8.88	13.36	10.34
		Standard error	1.75	1.78	1.8	1.78	1.83	1.86	1.73
	1997–2000	Mean	7.81	**10.36**	7.83	8.11	8.43	7.12	8.31
		Standard error	1.8	1.8	1.78	1.73	1.73	1.78	1.86
		% Change	−37	−26	−23	−19	−5	−47	−20
Fontana–Arrow Highway	1988–1991	Mean	10.41	**13.09**	9.8	9.77	8.6	11.81	9.53
		Standard error	1.68	1.71	1.68	1.61	1.63	1.71	1.61
	1997–2000	Mean	6.75	8.99	7.11	**9.06**	6.63	6.89	7.11
		Standard error	1.65	1.65	1.63	1.58	1.63	1.58	1.63
		% Change	−35	−31	−27	−7	−23	−42	−25
Ontario–Airport	1988–1991	Mean	10.96	**13.69**	11.68	10.16	9.93	11.99	11.67
		Standard error	1.57	1.55	1.55	1.57	1.57	1.59	1.59
	1997–2000	Mean	6.84	**9.24**	7.07	8.05	7.43	8.43	6.4
		Standard error	1.87	1.83	1.83	1.73	1.83	1.76	1.8
		% Change	−38	−33	−39	−21	−25	−30	−45
North Long Beach	1988–1991	Mean	5.59	5.85	**6.41**	5.42	5.28	4.1	4.09
		Standard error	1	0.99	1	0.96	0.96	1.02	0.99
	1997–2000	Mean	4.67	5.29	4.8	**5.76**	5.23	3.71	5.3
		Standard error	0.99	0.99	0.97	0.89	0.94	0.94	0.97
		% Change	−17	−10	−25	+6	−1	−10	+30
Azusa	1988–1991	Mean	6.62	6.36	**7.42**	6.5	6.78	6.8	6.35
		Standard error	1.06	1.01	1.04	1.01	1.03	1.03	1.03
	1997–2000	Mean	5.44	**7.13**	4.8	6.46	5.68	5.59	6.09
		Standard error	1.04	1.04	1	1.03	1.04	1.06	1.04
		% Change	−18	+12	−35	−1	−16	−18	−4
Burbank–West Palm Avenue	1988–1991	Mean	7.51	7.01	8.05	6.3	**8.53**	6.89	7.16
		Standard error	1	0.97	0.99	0.97	1	0.97	0.97
	1997–2000	Mean	5.03	**7.08**	5.36	6.27	5.29	6.01	5.45
		Standard error	1	1.02	0.97	0.96	0.96	0.99	0.96
		% Change	−33	+1	−33	0	−38	−13	−24
Lake Gregory	1988–1991	Mean	4.55	4.66	2.9	2.84	4.47	**4.71**	3.92
		Standard error	0.64	0.66	0.71	0.66	0.66	0.66	0.65
	1997–2000	Mean	2.41	2.36	3	2.36	2.31	2.12	**3.02**
		Standard error	0.54	0.58	0.57	0.54	0.53	0.57	0.54
		% Change	−47	−49	+4	−17	−48	−55	−23
Perris	1988–1991	Mean	7	7.95	6.84	7.92	5.01	**8.69**	5.88
		Standard error	1.26	1.29	1.27	1.34	1.29	1.31	1.22
	1997–2000	Mean	4.28	**6.88**	4.3	6.25	5.17	4.89	4.04
		Standard error	1.27	1.31	1.29	1.34	1.29	1.31	1.22
		% Change	−39	−14	−37	−21	+3	−44	−31
Riverside–Rubidoux	1988–1991	Mean	**16.87**	16.74	15.57	15.85	13.99	16.48	16.31
		Standard error	1.98	1.96	2.04	2.01	2.01	1.98	1.96
	1997–2000	Mean	9.31	**12.56**	9.77	11.45	10.69	8.74	10.37
		Standard error	1.88	1.79	1.79	1.73	1.88	1.79	1.75
		% Change	−45	−25	−37	−28	−24	−47	−36

Table 4. (cont.)

Site	Period		Day-of-Week Average PM_{10}-NO_3^- Concentration ($\mu g/m^3$) Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
El Toro	1988–1991	Mean	4.18	3.93	**4.98**	4.24	3.7	3.08	4.87
		Standard error	0.73	0.77	0.76	0.72	0.74	0.76	0.75
	1997–2000	Mean	3.66	**4.73**	4.04	3.34	3.99	3.65	3.59
		Standard error	0.79	0.8	0.81	0.79	0.79	0.79	0.8
		% Change	−13	+20	−19	−21	+8	+18	−26
Santa Clarita–County Fire Station	1988–1991	Mean	2.86	3.2	3.22	3.26	3.6	2.9	**4.16**
		Standard error	0.75	0.75	0.77	0.71	0.7	0.73	0.7
	1997–2000	Mean	2.65	3.1	2.61	2.78	2.25	**3.34**	2.78
		Standard error	0.6	0.61	0.62	0.58	0.59	0.59	0.61
		% Change	−7	−3	−19	−15	−38	+15	−33
Los Angeles–North Main Street	1988–1991	Mean	6.22	6.64	**7.94**	6.19	7.3	7.44	7.38
		Standard error	1.01	1.01	1.04	1.06	1.01	1	1.03
	1997–2000	Mean	5.64	6.48	5.11	**7.28**	5.86	5.42	6.3
		Standard error	1.04	1.04	1.03	0.98	0.98	1	0.98
		% Change	−9	−2	−36	+18	−20	−27	−15

Note: Boldface indicates highest day-of-week concentration. The difference between two means is significant if the absolute difference is greater than the following: $t_{crit} \times \text{sqrt}(SE_1^2 + SE_2^2)$, where t_{crit} is based on at least 30 degrees of freedom, and SE indicates standard error. Means and their standard errors were prepared using the LSMEANS option in SAS PROC GLM for each location separately.

the $PM_{2.5}$ mass data. The weekend averages are generally lower than weekday averages for nitrates, sulfates, organic carbon, and elemental carbon. Because heavy-duty trucks typically represent a major source of elemental carbon, the Sunday decrease in heavy-duty truck travel may also result in a decrease in ambient elemental carbon concentrations.

- Day-of-week patterns of the CADMP-$PM_{2.5}$ data follow relatively the same pattern as NO_x and CO data. This similarity, combined with the facts that the vast majority of CO emissions and the much of the NO_x emissions come from light-duty vehicles, indicates that motor vehicles, whether by direct emissions, re-entrainment processes, or secondary formation from gaseous emissions, contribute appreciably to ambient PM concentrations in California.

In summary, analysis of PM concentrations indicates a general weekly pattern with the maximum occurring late in the workweek and the minimum occurring on weekends (especially Sunday); however, the pattern is not statistically significant at all sites and areas. Given the wide variety of sources contributing to PM and the factors listed previously, interpretation of these results in terms of weekday/weekend emissions differences is complex and should be done with caution. More hourly PM data and a more comprehensive air quality data analysis, as well as a three-dimensional modeling study testing the impact of changes in emission levels, timing, spatial distributions, and so on, would lead to a more accurate characterization of the weekday/weekend pattern of PM and the major contributing factors.

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